



Baseline Assessment of Petroleum Contamination and Soil Properties at Contaminated Sites in Utqiagvik, Alaska

Robyn A. Barbato, Stacey L. Jarvis, Karen L. Foley, and Robert M. Jones

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tion Study (Bench Scale) in Utqiagvik Alaska"

Abstract

Elevated contamination levels persisted for decades at the former Naval Arctic Research Station at two sites in particular, the Airstrip and Powerhouse sites. Because of the challenging environmental conditions at these sites, physical and chemical remediation technologies have not been effective at reducing petroleum contamination levels. Therefore, the continued presence of the contamination warranted a deeper investigation of petroleum chemistry, soil attributes, and biological activity at these sites. Petroleum chemistry analysis revealed the heterogeneous contamination at each site, with higher levels observed at the upgradient sites, which were situated further from the nearby freshwater Imikpuk Lake. Additionally, soil biological data tests showed an active microbial community, including high bacterial numbers in these soils. The results from this baseline study indicate that stimulating biodegradation processes in petroleum-contaminated soils is a promising technology for bioremediation.

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Preface

This study was conducted for the Naval Facilities and Engineering Command (NAVFAC) under MIPR N6247315MPT0010, "Conduct Hydrological Study, Ultraviolet Optical Screening Tool (UVOST) Study, Thermal Scale, Thermal Study, and Bioremediation Study (Bench Scale) in Utqiagʻvik Alaska." The technical monitor was Ms. Kendra Leibmen, NAVFAC.

The work was performed by the Biogeochemical Sciences Branch (CEERD-RRN) of the Research and Engineering Division (CEERD-RR), ERDC-CRREL. At the time of publication, Dr. Justin Berman was Chief, CEERD-RRN; CDR J. D. Horne, USN (Ret), was Chief, CEERD-RR; and Dr. Mark L. Moran, CEERD-RZT, was the ERDC-CRREL Technical Director. The Deputy Director of ERDC-CRREL was Dr. Lance D. Hansen, and the ERDC-CRREL Director was Dr. Joseph L. Corriveau.

We would like to thank Mr. Art Gelvin for Global Positioning of sample collation locations and for Figures 3 and 4, Dr. Anna Wagner and Mr. Kevin Bjella for UVOST data, and Ms. Flora Cullen for significant contributions to the plant viability analysis.

COL Bryan S. Green was Commander of ERDC, and Dr. David W. Pittman was the Director.

Acronyms and Abbreviations

ADEC Alaska Department of Environmental Conservation

AS Airstrip

ATCC American Type Culture Collection

BTEX Benzene, Toluene, Ethylbenzene, Xylene

CaCl₂ Calcium Chloride

CO₂ Carbon Dioxide

CRREL Cold Regions Research and Engineering Laboratory

DG Downgradient

DNA Deoxyribonucleic Acid

DUP Duplicate

EPH Extractable Petroleum Hydrocarbon

ERDC U.S. Army Engineer Research and Development Center

FID Flame Ionization Detector

GC Gas Chromograph

GWC Gravimetric Water Content

HAVE Hot Air Vapor Extraction

JP-5 Jet Petroleum

LIF-UVOST Laser Induced Fluorescence-Ultraviolet Optical Screening Tool

LOI Loss on Ignition

MBTE Methyl Tertiary Butyl Ether

MDEP Massachusetts Department of Environmental Protection

NARL Naval Arctic Research Laboratory

NAVFAC Naval Facilities and Engineering Command

PH Powerhouse

PID Photoionization Detector

qPCR Quantitative Polymerase Chain Reaction

rRNA Ribosomal Ribonucleic Acid

TPH Total Petroleum Hydrocarbons

UG Upgradient

UIC Ukpeaġvik Iñupiat Corporation

USEPA Environmental Protection Agency

UVOST Ultraviolet Optical Screening Tool

VPH Volatile Petroleum Hydrocarbon

1 Introduction

1.1 Background

From the mid-1900s through 1987, scientific research was conducted at the former Naval Arctic Research Laboratory (NARL), located in Utqiagʻyik (formerly Barrow), Alaska. Activities at the former NARL resulted in contamination with multiple compounds, from polychlorinated biphenyls to petroleum compounds. In the late 1990s, the U.S. Navy, Ukpeagvik Iñupiat Corporation (UIC), and the Alaska Department of Environmental Conservation (ADEC) began developing a plan to clean up the contaminated sites at the former NARL (U.S. Navy 2002a, 2002b) (Figure 1). Elevated contamination levels persisted at two sites in particular, the Airstrip and Powerhouse sites, warranting further investigation starting in 1997 and long-term monitoring in 2003 (Figure 2). Monitoring activities showed elevated concentrations of petroleum in groundwater at both sites, likely caused by the austere conditions of the site, including the dry, cold climate and presence of permafrost. These environmental conditions further constrain technologies to remediate the petroleum contamination present at these sites. Therefore, unique technologies able to overcome the physical limitations of this system are necessary to clean up the contamination, particularly close to Imikpuk Lake, a freshwater lake in Utqiagvik, Alaska.

More recently, the Cold Regions Research and Engineering Laboratory (CRREL) assessed petroleum contamination at the Airstrip and Powerhouse sites by using Laser Induced Fluorescence-Ultraviolet Optical Screening Tool (LIF-UVOST) (U.S. Navy 2016). While LIF-UVOST detected the presence or absence of petroleum compounds at the site, this technology could not determine the type of petroleum constituent present. Therefore, these data, in conjunction with petroleum chemistry data from 2012, were used to identify select locations for further investigation of petroleum compounds.

Figure 1. Study sites in Utqiagʻvik, Alaska: (a) map of Alaska, (b) both sites adjacent to Imikpuk Lake, (c) Airstrip site northeast of Imikpuk Lake, and (d) Powerhouse site west of Imikpuk Lake. (Map data from Google, DigitalGlobe 2017.)

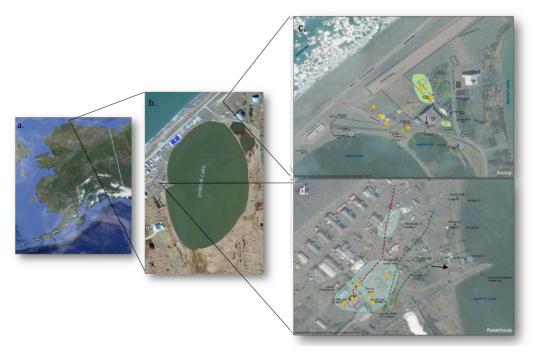
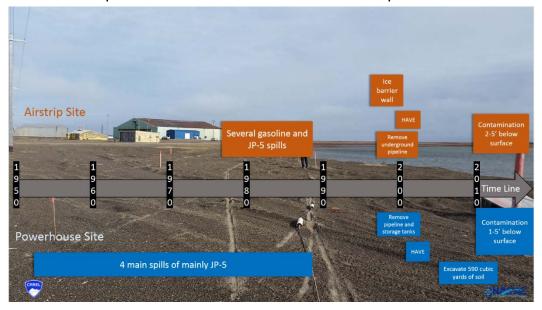


Figure 2. Select episodes of contaminant introduction and cleanup technologies. The approximate timeline shows known events contributing to petroleum contamination at the Airstrip and Powerhouse sites. *HAVE* indicates hot air vapor extraction.



1.2 Objective

The objective of our baseline soil survey was to conduct an in-depth analysis of the fractions of petroleum hydrocarbons and microbial activity in

situ to reveal the status of each site at the time of sampling. The goal was to use the results of this study as guidance for the bench-scale and pilot-scale remediation efforts planned at these sites.

1.3 Approach

Bioremediation is of particular interest because the remote nature and extreme temperatures of the site limit traditional treatments that require personnel or heavy machinery and in turn become costly and logistically challenging. Bioremediation is a remediation technology whereby organisms, mainly microbes, are stimulated to break down contaminants of concern into innocuous end products. In recent years, phytoremediation (using plants to stimulate bioremediation) has been found to be a cost-effective and noninvasive method of contaminant clean up (Pilon-Smits 2005). Larger, more complex molecules, such as petroleum constituents, require microbial enzymes to break down the complex chain and ring structures.

Therefore, bioremediation is a promising technology to accelerate degradation of petroleum hydrocarbons under the challenging conditions found at the former NARL sites in Utqiaʻgvik, Alaska. The specific aim of this study was to determine the baseline characteristics of up- and downgradient areas within the Airstrip and Powerhouse sites at the Former NARL in Utqiaʻgvik, Alaska. To achieve this, our approach was to collect soil samples in areas of known contamination of petroleum constituents. Those samples were analyzed for petroleum concentrations in addition to the physical and microbial soil attributes within the soil samples collected. These data informed the next phase of the study to test effective remediation techniques on soils collected in these contaminated areas.

2 Site Overview

2.1 Former NARL facility

The former NARL facility is approximately 6.4 km northeast of the village of Utqiagvik and 9.6 km southwest of Point Utqiagvik, the northernmost point of Alaska. The NARL facility is bordered by the Chukchi Sea to the west, the Arctic Ocean to the north, and the Beaufort Sea to the east. Originally, the facility opened in 1947 to enable exploration of petroleum in the High Arctic and then was used as a Navy operation center in the Arctic. Forty years later, ownership was transferred from the Navy to the UIC, a Utqiagvik native village corporation. Currently, the former NARL is operated by UIC and houses Ilisagvik College and office space.

2.2 Airstrip site

The Airstrip site is located at the former NARL, about 6 km north of Utqiagvik and 250 m inland from the shoreline of the Arctic Ocean. It covers approximately 500,000 m² and includes a 1520 m runway, a large hangar, an apron area, and other buildings. Marston Matting was placed on the runway and apron to promote a stable soil surface. There are two layers of this joint steel-plate matting on the apron; and it serves as a physical barrier but inhibits easy access to deeper soil horizons where the petroleum constituents may reside.

While in operation, fuel spills totaling approximately 1,386,000 L of fuel were reported at this site. Between 1976 and 1986, gasoline and jet petroleum (JP-5) fuel spills occurred. Specifically, an underground fuel line failed (183,000 L of gasoline), and a valve was left open (94,000 liters of JP-5). Additional activities resulted in the release of 1,050,000 L of gasoline and 61,000 L of JP-5, with some recovery of 530,000 L of gasoline and 4000 L of JP-5.

This site has been monitored for gasoline range organics, diesel range organics, and volatile organic compounds. Long-term monitoring started in 2003 to evaluate natural attenuation of the petroleum compounds at the site, with two 5-year reviews (U.S. Navy 2008, 2013a). In response to excessive concentrations of petroleum compounds in the active layer, further evaluation in 2012 showed the location and magnitude of petroleum compounds (U.S. Navy 2013b).

Some remediation activities at this site included the removal of 1340 m of an underground fuel pipeline (U.S. Navy 1997) and construction of a recovery trench and artificially raised permafrost table. Further removal of gasoline and diesel in these contaminated soils occurred by hot air vapor extraction (HAVE) between 2000 and 2002 (U.S. Navy 2003). After treatment, soil was returned to the excavation areas.

2.3 Powerhouse site

The Powerhouse site is located at the former NARL, approximately 300 m inland from the shoreline of the Arctic Ocean. The former powerhouse, inactive water pump house, and the UIC Construction equipment lay-down area are present at the Powerhouse site. From 1952 to 1988, approximately 95,000 L of JP-5 were released.

Remedial activities included removal of a pipeline in 1997 that connected to the Airstrip site, aboveground storage tanks in 2000, and excavation of soil (300 m³) in 2000. Long-term monitoring commenced in 2004 to monitor the water in the active zone and on the surface for petroleum compounds.

2.4 Site characteristics

The majority of the ecosystem is tundra with native plant species of *Eriphorum angustifolium*, *Carex aquatilis*, and *Dupontia fischeri* (Shaver and Billings 1975). The climate has been described as a polar desert due to cold temperatures and lack of humidity. The average high temperature during the summer months is 7°C (Clebsch 1968), though temperatures in Utqiaġvik can range from –28.3°C in February to 4.4°C in July. The growing season occurs between mid-June and late August, with maximum permafrost thaw measured at 30 cm in 1975 (Shaver and Billings 1975). Permafrost exists at various depths throughout the landscape. The tundra microtopography will likely be sensitive to climate impacts in the near term (Liljedahl et al. 2016).

The former NARL site was engineered with fill, resulting in a sand and gravel soil composition at both the Airstrip and Powerhouse sites. These soils are very large grained, nutrient poor, and contaminated with petroleum hydrocarbons. During sample collection, tundra was observed at a depth of approximately 0.5 m at the Powerhouse site. At the Airstrip site, the depth of fill was greater than 0.5 m at the areas sampled. Thus, no

tundra was observed. In August 2016, qualitative assessment suggested that samples collected near the shore of Imikpuk Lake contained a higher fraction of gravel when compared to the soils from the upgradient areas. The upgradient areas were positioned farther from the lake than the downgradient areas.

3 Soil Collection

During a field campaign from 16 to 23 August 2015, we collected soil samples from select locations within the up- and downgradient areas at the Airstrip (Figure 3) and Powerhouse (Figure 4) sites. The overall goals of this study were to (1) characterize the soil properties of the site, (2) quantify the current concentrations of discrete petroleum fractions, and (3) determine the extent of microbial activity to develop a baseline index of biochemical properties. At each site, downgradient areas were classified by their proximity to Imikpuk Lake and the high water table whereas upgradient areas were classified by their high contamination levels of total petroleum hydrocarbons (TPH) and farther distance from the lake. Specific sample areas were selected based on 2012 and 2015 LIF-UVOST survey results that identified areas of high concentrations of TPH. Sampling depths were determined by previous sampling efforts and near-real-time UVOST data. Specifically, during the 2012 UVOST investigation, petroleum was detected at the following depths: 0.6 to 1.5 m and 0.3 to 1.5 m at the Airstrip and Powerhouse sites, respectively (U.S. Navy 2016). Water tables were high at the downgradient sites, which was further supported by our observations of elevated moisture levels in those particular samples. Table 1 summarizes the sampling location depths for each location.

Baseline samples were collected in the field to be analyzed to determine the concentration of petroleum fractions as measured by volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) present at the Airstrip and Powerhouse sites. Six samples per upgradient area and two samples per downgradient area were collected. Samples from these sixteen locations were also sent back to CRREL to be analyzed for soil properties, DNA (deoxyribonucleic acid), and microbial attributes.

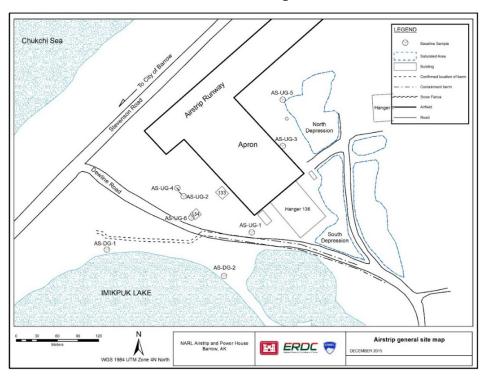


Figure 3. Airstrip sampling locations. *AS* indicates Airstrip, *UG* indicates upgradient, and *DG* indicates downgradient.

Figure 4. Powerhouse sampling locations. *PH* indicates Powerhouse, *UG* indicates upgradient, and *DG* indicates downgradient.

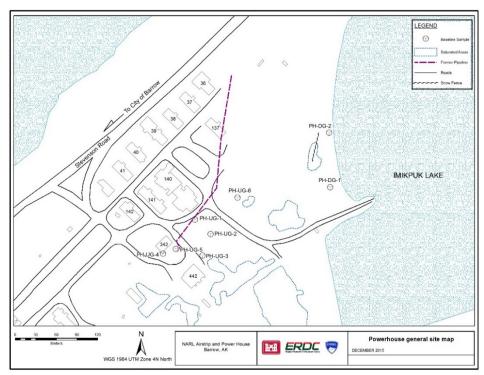


Table 1. Field sampling identifiers and collection
depths: Airstrip (AS), Powerhouse (PH), and up- (UG)
and downgradient (DG) sample locations.

Sample	UVOST 2012 Designation	Sampling Depth (m)
AS-UG-1	AS4-B2	0.91
AS-UG-2	AS1-B4	1.07
AS-UG-3	AS2-B6	1.07
AS-UG-4	AS1-B3	1.07
AS-UG-5	AS2-B8	0.61
AS-UG-6	AS-UV-65	1.07
AS-DG-1	AS-WP-02B	0.46
AS-DG-2	AS-UV-27	0.46
PH-UG-1	PH4-B9	1.07
PH-UG-2	PH4-B10	0.91
PH-UG-3	PH4-B8	0.61
PH-UG-4	PH4-B6	0.46
PH-UG-5	PH4-MW-02B	0.76
PH-UG-6	PH-WP-06B	0.15
PH-DG-1	PH1-B1	0.46
PH-DG-2	PH1-B2	0.30

Specifically, at each sampling location, a gas-powered hydraulic Earth Drill (Little Beaver HYD-TB11H, Livingston, TX) was used to drill a hole to just above the sampling depth (Figure 5). From there, a hand-operated auger with removable plastic sleeves was used to access the sampling depth and prevent extraneous sample disturbance. From the sampling sleeves within the auger, soil was collected for a baseline soil analysis of VPH and EPH by using methanol-washed stainless-steel tools. For the VPH samples, approximately 5 g of soil was transferred to a sterile 40 ml amber glass vial prepreserved with purge-and-trap-grade methanol. For EPH samples, approximately 25 g of soil was transferred to a sterile 4 oz amber glass jar and sealed. All samples were sealed with parafilm and immediately placed on ice until they could be sent for chemical analysis to Fremont Analytical, Inc. (Seattle, WA). Subsamples were aseptically collected for soil properties, such as moisture content, pH, and carbon content, and for microbial analyses. Aseptic soil collection included rinsing the collection tools with 70% isopropanol and DNase and RNase solutions. Samples were placed on ice, shipped, and stored at 4°C for respiration analysis or at -80°C for molecular analysis until processed.

ERDC/CRREL TR-17-13

Figure 5. Drilling equipment. Field setup of (a) the drilling apparatus and (b) the auger.

a)



4 Sample Analyses

4.1 Soil property analyses

4.1.1 Gravimetric water content (GWC)

The mass of a soil sample was measured at room temperature, the sample was heated in an oven at 105° C for 24 hours, and the mass was measured again. Percent GWC was calculated according to the formula below. Mass is indicated by m.

$$GWC = \frac{(m \ wet \ soil) - (m \ dry \ soil)}{m \ dry \ soil} * 100$$

4.1.2 Soil pH

Approximately 10 g of each air-dried soil sample was added to individual vials followed by the addition of 10 mL of deionized water, and the slurry was mixed well. After allowing the soil particles to settle, approximately 10 minutes, the soil pH was measured at 23°C using a three-point calibration with a pH probe (Hanna Instruments) connected to a Mettler Todelo meter (Seven Easy). Then, 0.1 mL of a dilute salt (1 M CaCl₂ [calcium chloride]) was added to the vial containing soil and water; the soil slurry was mixed well and then allowed to settle for 10 minutes. Soil pH was then measured as occurred with the deionized water.

4.1.3 Soil carbon through loss on ignition

Soil previously dried for gravimetric water content was then heated in a muffle furnace at 360°C for 2 hours, and the mass was immediately measured once the temperature dropped below 150°C.

Percent carbon loss on ignition (LOI) was calculated with the following formula. Mass is indicated by *m*.

$$LOI = \frac{(m \text{ at } 105^{\circ}\text{C}) - (m \text{ at } 360^{\circ}\text{C})}{m \text{ at } 105^{\circ}\text{C}} * 100$$

4.2 Biological properties analyses

4.2.1 Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID) headspace analysis

To estimate soil microbial activity, evolution of carbon dioxide (CO₂) over a specific incubation period was measured using a GC-FID. Approximately 10 g of soil were placed in a glass vial and sealed using a siliconelined septum and aluminum crimp cap. The time each vial was sealed was noted. All vials were then incubated at 7°C for 48 hours. The headspace gas of each soil sample was then analyzed on the GC-FID using an autosampler designed for headspace gas analysis. Concentration of CO₂ evolved was calculated in μ g C-CO₂ g dry soil-1 day-1.

4.2.2 DNA extraction

Genomic DNA was extracted from approximately 0.50 g of soil by using the MoBio PowerSoil DNA extraction kit (Carlsbad, CA). DNA concentrations were quantified by using the NanoDrop 2000 UV-Vis Spectrophotometer (Thermo Scientific, Wilmington, DE). DNA was diluted with sterile, DNA-free water to achieve 20 ng per quantitative polymerase chain reaction (qPCR).

4.2.3 Quantitative PCR

We amplified the bacterial 16S rRNA (ribosomal ribonucleic acid) genes by using primers 331F and 797R and probe BacTaq (Nadkarni et al. 2002). All qPCR reactions were conducted in duplicate on the Lightcycler 480 System (Roche Molecular Systems, Inc., Indianapolis, IN). The 20 µL reaction volumes included 20 ng DNA, 10 µM of primers, 5 µM of probe, and 10 μL of Lightcycler TaqMan Master Mix (Roche Molecular Systems, Inc., Indianapolis, IN). We prepared standards for qPCR by using genomic DNA from *Pseudomonas fluorescens* obtained from the American Type Culture Collection (ATCC, Manassas, VA) and grown according to ATCC's recommended protocol. Once the culture reached log phase growth, we conducted plate or microscopic counts and isolated DNA from the cultures by using the Microbial DNA Isolation Kit (MoBio Laboratories, Carlsbad, CA). Genomic DNA was quantified using the NanoDrop 2000 UV-Vis Spectrophotometer (Thermo Fisher Scientific, Inc., Wilmington, DE) with the assumption of six copies of the 16S rRNA gene per genome for *P. fluo*rescens (Fogel et al. 1999; Bodilis et al. 2012). We optimized the following

cycling parameters for bacterial qPCR: 95° C for 600 s followed by 45 cycles of 95° C for 30 s, 57° C for 60 s, and 72° C for 25 s with final extension at 40° C for 30 s.

4.3 Methods to quantify petroleum hydrocarbon fractions

4.3.1 Volatile petroleum hydrocarbons (VPH)

We analyzed the samples by using purge-and-trap sample concentration. The gas chromatograph was temperature programmed to facilitate separation of organic compounds. Detection was achieved by a photoionization detector (PID) and flame ionization detector (FID) in series. Quantitation was based on comparing the PID and FID detector response of a sample to a standard composed of aromatic and aliphatic hydrocarbons. We used the PID chromatogram to determine the individual concentrations of targeted analytes (BTEX/MTBE—benzene, toluene, ethylbenzene, xylene / methyl tertiary butyl ether) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12, and C12 through C13 ranges. The FID chromatogram was used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10, and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations were subtracted from the FID concentrations to yield the aliphatic ranges values. This method is suitable for the analysis of waters, soils, and sediments. Soil samples dispersed in methanol were combined with water for purging directly from a soil purge vessel (EPA method 5035). Figure 6 highlights aliphatic and aromatic fractions as measured by VPH that were considered for our reporting.

The method used in this study to quantify VPH fractions was modified and adapted from the "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)," Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection (MDEP) and on U.S. Environmental Protection Agency (USEPA) method 5035. The MDEP in turn based their method on (1) USEPA Methods 5030, 8000, 8020, and 8015 from SW-846, *Test Methods for Evaluating Solid Waste* (USEPA 1986e, 1986a, 1986b, 1986c), and (2) *Method for Determining Gasoline Range Organics* from the Wisconsin Department of Natural Resources (1995a).

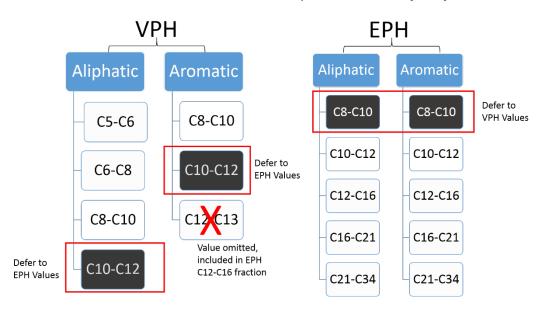


Figure 6. Aliphatic and aromatic fractions measured by each petroleum hydrocarbon method.

This identifies the fractions used for the petroleum chemistry analysis.

4.3.2 Extractable petroleum hydrocarbons (EPH)

Samples submitted for EPH analysis were extracted into methylene chloride, dried over sodium sulfate, solvent exchanged into pentane and methylene chloride, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions were conducted using a modification of USEPA method 3630 (silica gel cleanup). The two extracts produced were then concentrated to final volumes of 1 mL each (i.e., an aliphatic extract and an aromatic extract) and were then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds was collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21, and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds was likewise collectively integrated within these ranges. Figure 6 highlights aliphatic and aromatic fractions as measured by VPH that were considered for our reporting.

Average calibration factors, or response factors, were determined using an aliphatic hydrocarbon standard mixture, which was used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor, or response factor, determined using the aromatic hydrocarbon standard mixture was used to calculate the collective concentrations of the aromatic hydrocarbon ranges.

The method used in this study to quantify EPH fractions is suitable for the analysis of waters, soils, and sediments and was modified and adapted from the Massachusetts Department of Environmental Protection's (MDEP 2004) *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)*. The MDEP in turn based their method on (1) USEPA Methods 8000, 8100, and 3630 from SW-846, *Test Methods for Evaluating Solid Waste* (USEPA 1986a, 1996d, 1996b) and (2) *Method for Determining Diesel Range Organics* from the Wisconsin Department of Natural Resource (1995b).

4.3.3 Percent moisture for hydrocarbon analysis

Approximately 10 g of soil was placed in a tin to obtain the mass of the wet soil sample. The sample was then dried for a minimum of 2 hours at 110°C, and then the mass of the dry soil sample was recorded once cooled. We then calculated the percent moisture by using the mass loss determined by comparing the wet and dry masses between each soil sample.

5 Baseline Study Results

5.1 Baseline soil properties

Gravimetric water content results showed low moisture in most of the soils collected at the Airstrip (AS) and Powerhouse (PH) up- (UG) and downgradient (DG) sites (Figure 7). Soil moisture was low due to the large particle sizes in those soils. Notable increases in moisture content occurred at AS-DG-1,2 and PH-UG-1, likely because a subsurface layer of tundra was sampled as well. In fact, there was standing water in those sample bags, which was mixed back into the sample before analysis. Tundra soils hold larger amounts of water than soils composed mainly of gravel or large sand particles. Additionally, tundra soils, namely AS-DG-2 and PH-UG-1, have higher organic matter levels due to the decomposed plant and shrub matter in these soils. The other soils contained lower amounts of organic matter (Figure 8). Soil pH was circumneutral, with slightly lower values in the tundra soils (Figure 9).

Figure 7. Baseline water content. Each bar represents one discrete sample. *AS* indicates Airstrip site, *PH* indicates Powerhouse site, *UG* indicates upgradient, and *DG* indicates downgradient. *GWC* represents gravimetric water content.

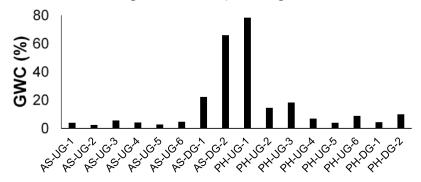
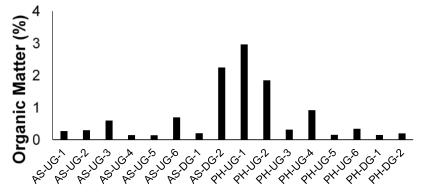


Figure 8. Baseline organic matter content as measured by loss on ignition. Each bar represents one discrete sample. *AS* indicates Airstrip site, *PH* indicates Powerhouse site, *UG* indicates upgradient, and *DG* indicates downgradient.



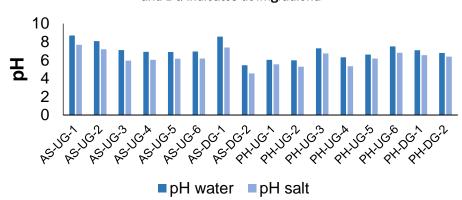


Figure 9. Baseline soil pH. Each colored bar represents one discrete sample. *AS* indicates Airstrip site, *PH* indicates Powerhouse site, *UG* indicates upgradient, and *DG* indicates downgradient.

5.2 Baseline petroleum hydrocarbon data

Aliphatic and aromatic petroleum fractions were quantified at select upand downgradient areas within the Airstrip (Figure 3) and Powerhouse (Figure 4) sites. We measured aliphatic chain lengths from C5 to C34 and aromatic ring structures from C8 to C34. By measuring fractions of petroleum hydrocarbons, we are able to not only determine the presence or absence of TPHs at the former NARL site but also characterize the specific groups of compounds that are persisting at the site. Data analysis from specific fractions is critical for site assessment purposes and for determining whether degradation is occurring over a given time period or according to a particular treatment technology.

Aliphatic hydrocarbons were detected in the downgradient areas within the Airstrip site from the C12–C16, C16–C21, and C21–C34 fractions and within the Powerhouse site in the C16–C21 and C21–C34 fractions. Aromatic hydrocarbons from the C16–C21 and C21–C34 fractions and the C10–C12, C12–C13, and C21–C34 fractions were detected in the downgradient areas within the Airstrip and Powerhouse sites, respectively. Most of these hydrocarbons were composed of either longer chains or more ring structures, suggesting the prevalence of more recalcitrant compounds within the DG areas.

In comparison, soils in the upgradient areas from both sites contained elevated concentrations of fractions of aliphatic and aromatic hydrocarbons (Figures 10–13). These values were expected because the sources of petroleum contamination occurred in and around the upgradient areas at both

sites. Furthermore, the soil and distribution of petroleum is heterogeneous, as evidenced by significant variability of specific petroleum fractions at nearby sample collects. Duplicates from a single field location, AS-UG-3, showed a difference of approximately 500 mg/kg dry soil in the aliphatic hydrocarbons in the range of C12–C16, highlighting the incredible environmental variability of these contaminants at these sites (Figure 10). This variability was further demonstrated at the Powerhouse site, though to a lesser extent. Specifically, aromatic hydrocarbon C21–C34 was almost an order of magnitude different between these duplicate samples (Figure 13).

Within the upgradient area of the Airstrip site, the concentrations of aliphatic hydrocarbon C12–C16 were the highest as compared to the other fractions, reaching to approximately 1250 mg per kg dry soil at one location. Also of note is the prevalence of aromatic hydrocarbon C10–C12 at AS-UG-3 and AS-UG-5 (Figure 11). Of particular interest is the persistence of aromatic hydrocarbon C21-C34 at AS-UG-6 and AS-DG-2 (Figure 11).

Figure 10. Concentrations of aliphatic hydrocarbon fractions from Airstrip baseline soils. Each bar represents one measurement from one sampling location. Colors show the specific aliphatic fractions measured. *DUP* indicates a duplicate soil sample collected from the same site as the rest of the name designation. *U* indicates not detected, and asterisks indicate estimated values.

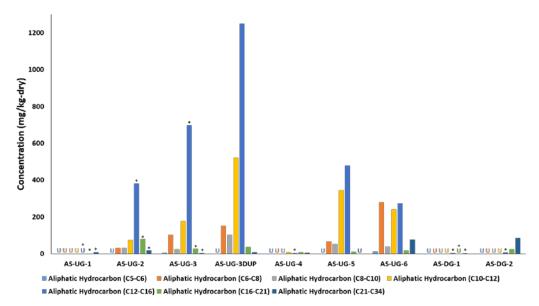


Figure 11. Concentrations of aromatic hydrocarbon fractions from Airstrip baseline soils. Each bar represents one measurement from one sampling location. Colors show the specific aromatic fractions measured. *DUP* indicates a duplicate soil sample collected from the same site as the rest of the name designation. *U* indicates not detected, and asterisks indicate estimated values.

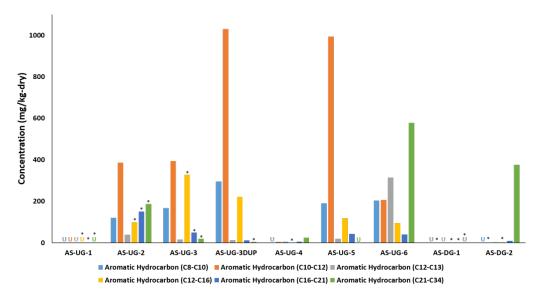


Figure 12. Concentrations of aliphatic hydrocarbon fractions from Powerhouse baseline soils. Each bar represents one measurement from one sampling location. Colors show the specific aliphatic fractions measured. *DUP* indicates a duplicate soil sample collected from the same site as the rest of the name designation. *U* indicates not detected, and asterisks indicate estimated values.

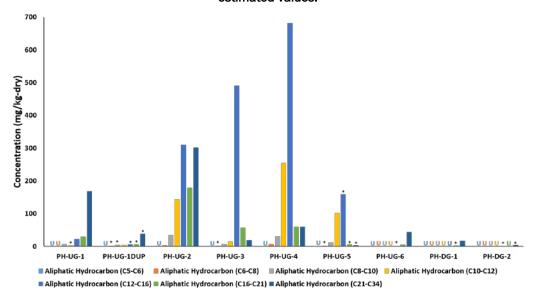
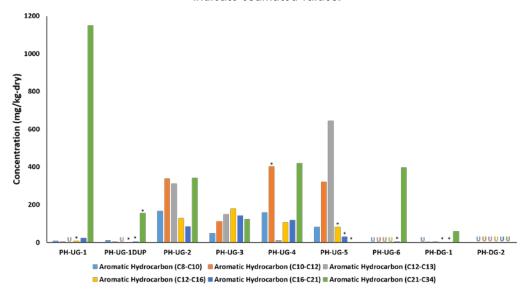


Figure 13. Concentrations of aromatic hydrocarbon fractions from Powerhouse baseline soils. Each bar represents one measurement from one sampling location. Colors show the specific aromatic fractions measured. *DUP* indicates a duplicate soil sample collected from the same site as the rest of the name designation. *U* indicates not detected, and asterisks indicate estimated values.



5.3 Baseline biological data

Both soil respiration rates and bacterial abundance are indicators of soil fertility at a given site. Soil respiration rates were generally quite low, likely due to the cold conditions and oligotrophic soils (Figure 14). Microbial respiration varied greatly across the baseline sample locations, even within a particular site, highlighting the spatial heterogeneity of soil organisms. Interestingly, the maximum respiration rates occurred at select sites in the upgradient areas (Figure 14). Though microbial activity ranged from less than 50 μ g C-CO₂ g⁻¹ dry soil day⁻¹ to approximately 1.8 mg C-CO₂ g⁻¹ dry soil day⁻¹, bacterial abundance did not change significantly. Therefore, either different microbes aside from bacteria are contributing to the elevated soil respiration rates or varying groups (e.g., phyla) of bacteria are affecting overall soil respiration rates. Bacterial abundance in general was comparable to temperate soils (Barbato et al. 2015) despite the extreme conditions of the site and the variable concentrations of petroleum hydrocarbons (Table 2).

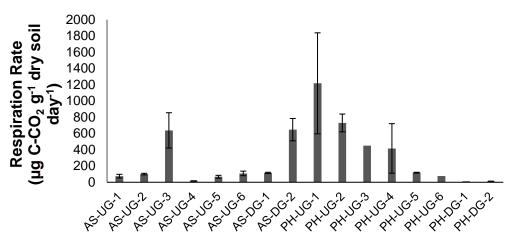


Figure 14. Average respiration rate by headspace analysis. Each bar is an average of two samples, and error bars show standard error.

Table 2. Bacterial abundance in baseline soils. This shows the bacterial abundance in soils collected from the downgradient (DG) and upgradient (UG) areas within the Airstrip (AS) and Powerhouse (PH) sites.

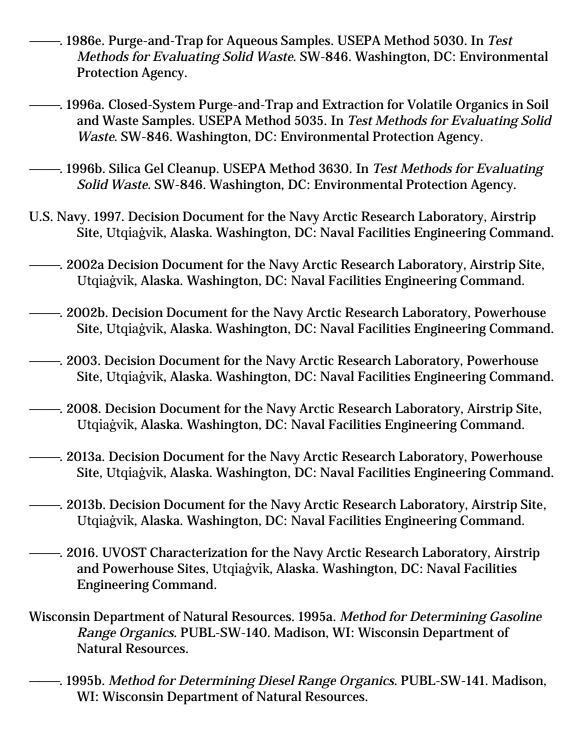
Sample ID	UVOST 2012 Designation	Bacterial Abundance (gene copies g ⁻¹ dry soil)
AS-DG-1	AS-WP-02B	3.12E+10
AS-DG-2	AS-UV-27	7.77E+09
AS-UG-1	AS4-B2	7.59E+09
AS-UG-2	AS1-B4	1.23E+10
AS-UG-3	AS2-B6	4.37E+10
AS-UG-4	AS1-B3	1.36E+10
AS-UG-5	AS2-B8	2.54E+10
AS-UG-6	AS-UV-65	3.35E+10
PH-DG-1	PH1-B1	4.14E+09
PH-DG-2	PH1-B2	2.42E+10
PH-UG-1	PH4-B9	1.45E+11
PH-UG-2	PH4-B10	1.47E+10
PH-UG-3	PH4-B8	2.93E+10
PH-UG-4	PH4-B6	2.40E+10
PH-UG-5	PH4-MW-02B	9.98E+10
PH-UG-6	PH-WP-06B	1.19E+10

6 Conclusion

Soils within downgradient areas at both NARL sites (Airstrip and Powerhouse) exhibited significantly lower concentrations of aliphatic and aromatic petroleum hydrocarbons than within upgradient sites, indicating that the contaminants have likely not reached soil near Imikpuk Lake. However, the aromatic hydrocarbons C21–C34 were in elevated concentrations at AS-DG-2, indicating the presence of heavy aromatics near the lake. In comparison, soils in the upgradient areas from both sites had elevated concentrations of fractions of aliphatic and aromatic hydrocarbons, indicating long-term presence of these contaminants and the need for implementation of remediation technologies to reduce contaminant concentrations. Soil biological data tests showed an active microbial community, particularly in the soils at the AS-UG-3, AS-DG-2, and PH-UG-1-4 sites, despite generally low soil respiration rates. Further evidence includes high bacterial numbers in these soils. The results from this baseline study indicate that there is continued presence of petroleum hydrocarbons at the Airstrip and Powerhouse sites. The presence of microbiota in the soil serve as promising indications that biodegradation processes could be stimulated in these petroleum-contaminated soils through bioremediation and phytoremediation technologies.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

Elevated contamination levels persisted for decades at the former Naval Arctic Research Station at two sites in particular, the Airstrip and Powerhouse sites. Because of the challenging environmental conditions at these sites, physical and chemical remediation technologies have not been effective at reducing petroleum contamination levels. Therefore, the continued presence of the contamination warranted a deeper investigation of petroleum chemistry, soil attributes, and biological activity at these sites. Petroleum chemistry analysis revealed the heterogeneous contamination at each site, with higher levels observed at the upgradient sites, which were situated further from the nearby freshwater Imikpuk Lake. Additionally, soil biological data tests showed an active microbial community, including high bacterial numbers in these soils. The results from this baseline study indicate that stimulating biodegradation processes in petroleum-contaminated soils is a promising technology for bioremediation.

15. SUBJECT TERMS

Arctic regions, Bioremediation, Contamination, Degradation, Hydrocarbons, Microorganisms, Oil pollution of soils, Permafrost, Petroleum, Utqiagvik Alaska

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